

Per- and Polyfluoroalkyl Substances (PFAS) Remediation Workshop

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Agenda

Introduction to Workshop and Objectives – Dennis Keane General audience questions Properties, Uses, Occurrence and Concerns with PFAS – Ellen Moyer Exercise 1 PFAS Remedial Options for Source and Plume Areas – Mike Marley Exercise 2 Break (5 minutes) Integrating Key Data in the Characterization Phase – Mike Marley Exercise 3 Exercise 4 Adsorption Case Studies – Mike Marley Exercise 5 Chemical Oxidation Case Study – Raymond Ball Wrap-Up / Summary of Current State of the Practice – Mike Marley

Additional Discussion – Dennis Keane



Overview

- ☐ New and fast-changing targets
 - ➤ Which PFAS?
 - ➤ Which cleanup levels?
 - ➤ Can we measure all PFAS?
- ☐ PFAS remediation challenges
 - ➤ Low cleanup levels
 - ➤ Numerous PFAS chemicals are all being or need to be remediated?
 - ➤ Transformation vs. destruction/mineralization
 - ➤ Risk of making things worse or not remediating adequately?
 - ➤ Are waste management issues fully understood and addressed?
- ☐ To help address issues
 - ➤ Collect appropriate site characterization data
 - ➤ Perform treatability and/or pilot testing



Properties, Uses, Occurrence and Concerns with PFAS



What are PFAS?

- ☐ Per- and polyfluoroalkyl substances
- ☐ A diverse class of synthetic chemicals in which at least one C is fully fluorinated
- ☐ C-F bonds are the shortest and strongest covalent bonds in nature
- ☐ Believed to be ~6,000 PFAS so far



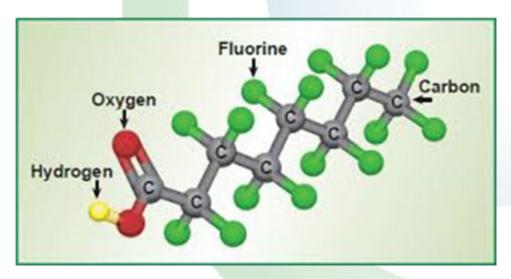
What are PFAS?

- ☐ Carbon chains with attached F
 - >2 to 18 C
 - ➤ Per FAS all C in the chain are bonded to F
 - Most desired manufactured chemicals are per
 - ➤ Poly FAS not all C in the chain are bonded to F
 - Most polys are unintended byproducts of manufacturing
 - Many are "precursors" to pers
- ☐ Other atoms can include O, H, S, N, others



What are PFAS?

- ☐ Produced in the largest amounts in the US:
 - Perfluorooctanoic acid PFOA (C8)
 - Perfluorooctane sulfonate PFOS (C8)
- ☐ PFAS properties:
 - > Water soluble
 - > Low volatility
 - Many resist biodegradation



NIEHS - National Institutes of Health

PFOA



Uses

- ☐ PFAS resist heat, oil, grease, and water
- □ Used in industry and consumer products worldwide since the 1950s − products contain a mix of carbon lengths and impurities
- ☐ Waterproof clothes, non-stick cookware, take-out containers
- Wire insulation
- Paper and paints
- ☐ Fire-fighting foams
- ☐ Carpet
- ☐ Furniture



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Physical-Chemical Properties

<u> </u>							
Property	PFOA	PFOS	Benzene				
Chemical Formula	$C_8HF_{15}O_2$	C ₈ HF ₁₇ O ₃ S	C_6H_6				
Molecular Weight (g/mol)	414.09	500.13	78.11				
Boiling Point (°C)	192.4	259	80				
Vapor Pressure (mm Hg at 25 °C)	0.525	~0.002	86				
Henry's Law Constant @ 25°C (unitless)	Not measurable	Not measurable	0.225				
K _{oc} (temperature as specified)	115	371	79 (at 25 °C)				
Solubility in Water (mg/L)	~9,500 (at 25 °C)	680 (temp. not stated)	1,780 (at 25 °C)				
	USEPA 2016	USEPA 2016					



Physical-Chemical Properties of Select Short-Chain PFAS

Property	CAS	Water solubility (mg/L)	Mp/Bp (°C)	Vapour pressure (Pa)	Log Pow	Log Koc
PFOS, perfluorooctane sulfonic acid	1763-23-1	519-570		3.31X10-4	5.5-7.03	2.57-3.3
PFOA, perfluorooctanoic acid	335-67-1	3400		12.1	3.6	2.11
PFHxS, perfluorohexane sulfonic acid	355-46-4	243.4	190/452	1.08x10-6	2.2	3.36/2.14
PFHxA, perfluorohexanoic acid	307-24-4	29.5 <<29		121	2.51 3.12-3.26	
PFHxA, perfluorohexanoate, sodium salt	2923-26-4	29.5		~ 0	0.70	
PFPeS, perfluoropentane sulfonic acid	2706-91-4					
PFPeA, perfluoropentanoic acid	2706-90-3	120			1.98	
PFBS, perfluorobutane sulfonate, potassium salt	29420-49-3	4340	188/447	1.49x10-6	0.26	2.25/1.07
PFBA, perfluorobutanoic acid	375-22-4	447			1.43	
8:2 FTOH, fluorotelomer alcohol	678-39-7	0.2 - 0.3		1.64	5.58	4.13
6:2 FTOH, fluorotelomer alcohol	647-42-7	19		22.1	4.54	2.43
4:2 FTOH, fluorotelomer alcohol	2043-47-2	97	-44/113	1330	3.07/3.30	2.34/2.83
6:2 FTS, fluorotelomer sulfonamide	27619-97-2				3.47-3.98	
6:2 FTAC, fluorotelomer acrylate	17527-29-6	0.38		44.3	5.2	



PFAS – Historical Timeline



When	What Happened
1950s	3M was first to produce PFOS and higher homologues
1969	AFFF was patented as a method for extinguishing liquid hydrocarbon fires and implemented by the DoD in 1969
1980s - 90s	First LCMSMS instruments with ppm to ppb detection capabilities
1990s	A handful of commercial labs developed propriety methods to meet client needs
2002	Global manufacturers began to replace LC PFCs with SC PFCs
2005	\$235Mil class action lawsuit brought by citizens against DuPont over PFC contamination in the Ohio river
2000s	LCMSMS technology advancements lead to ppt and ppq DLs.
2008, 09	EPA published Method 537 and Method 537 Version 1.1
2011	EPA published Draft Procedure for Analysis of PFCA and PFSA in Sewage Sludge and Biosolids by HPLC/MS/MS
2012	UCMR3 was signed by the EPA administrator
2014	ASTM Published Method D7968-14 for PFC in Soil by LC/MS/MS
2015	ASTM Published Method D7979-15 for PFC in Water, Sludge, Influent, Effluent and WW by LC/MS/MS

Primary Sources – Point or Direct



- Released in large quantities from primary manufacturing facilities
- Secondary Manufacturing incorporation of PFC raw materials into industrial and consumer products
- The use of AFFFs to fight fires is a direct pathway to the environment – (Connection to DoD)





Secondary Sources - Indirect



- Commercial and consumer products have a finite lifetime.
 - Dispose to landfills
 - > WWTP
 - Air emissions
- Trace chemistry transformation mostly degradation byproducts (TOP Assay)





Occurrence

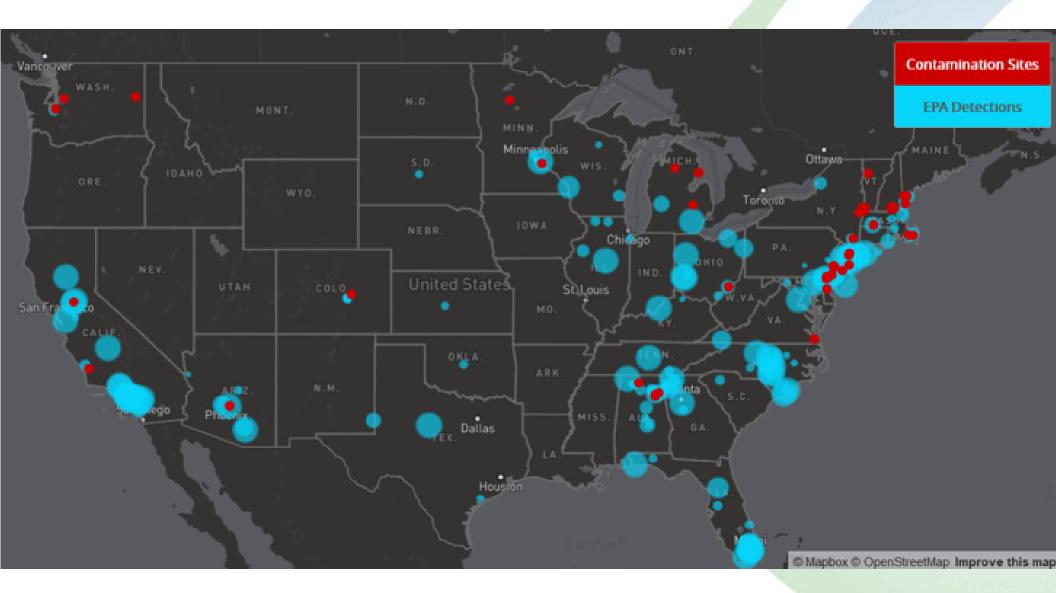
- ☐ Found worldwide in soil, air, water, wildlife, and humans
 - ➤ Including the Arctic and Antarctic
- □ 2015 study by U.S. National Health and Nutrition Examination Survey:
 - > PFAS found in 97 percent of human blood samples
- □ 2013-2015 Safe Drinking Water Act testing:
 - > PFAS found in 66 water supplies serving more than 16 million Americans in 33 states with at least one sample at or above EPA drinking water health advisories
- ☐ Tendency for large dilute plumes
- ☐ Difficult to sample
 - Cross-contamination issues
- ☐ Difficult to laboratory analyze
 - Some PFAS not detected by commercial labs



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PFAS in Tap Water and at Industrial and Military Sites



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Concerns

- ☐ Most attention with longer-chain PFAS (C8 or greater e.g., PFOA, PFOS)
- ☐ Persist, travel long distances, and bioaccumulate
- ☐ Potential health effects being studied:
 - ➤ Affect developing fetus and child including learning and behavior
 - Decrease fertility
 - Disrupt hormones
 - > Increase cholesterol
 - Suppress immune system
 - > Increase cancer risk





PFAS – Regulatory Timeline



When	Who	What Happened
1980s	EU	Groundwater directive to prevent discharge of PFOS
2002	US EPA	Initiated voluntary phase out of PFOS
2002	ЗМ	Discontinued making PFOS (7 other makers complied)
2006	US EPA	Announced 2010 (95%)/15(100%) PFOA Stewardship Program
2008	Canada	Regulated and prohibited PFOS imports to Canada
2009	UN	Stockholm Convention - adds PFOS to Annex B
2010	US EPA	2010 PFOA Stewardship program - must reduce PFOA use by 95%
2013	Canada	Use of AFFF with PFOS > 0.5ppm are prohibited
2013	DuPont	Makes a statement that it does not make, buy or use PFOS
2015	US EPA	Must 100% eliminate the use of PFOA by December 31,2015
May 2016	US EPA	PFOS and PFOA life time health limits reduced to 70 ppt each or the total if both are present.

Input from Dr. Jimmy Seow Dept. of Environment and Conservation Western Australia.





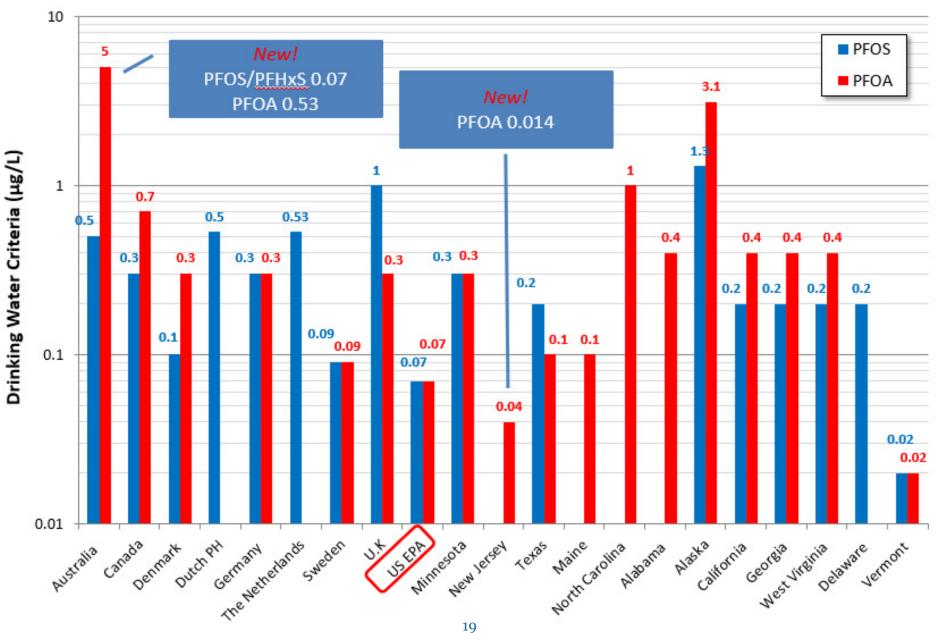
Standards and Guidelines

- ☐ EPA established health advisories for PFOA and PFOS
 - > 70 ng/L or ppt (individually and combined)
 - > For lifetime exposure from drinking water)
 - ➤ Based on lab studies of effects on rats and mice and epidemiological studies of exposed human populations
 - > EPA has no plans to establish Maximum Contaminant Levels
 - > EPA plans to develop Regional Screening Levels for site cleanup
- ☐ Other requirements vary widely
 - Some states and countries are looking at more than PFOA and PFOS
 - ➤ In the absence of federal MCLs, state standards lack enforcement teeth





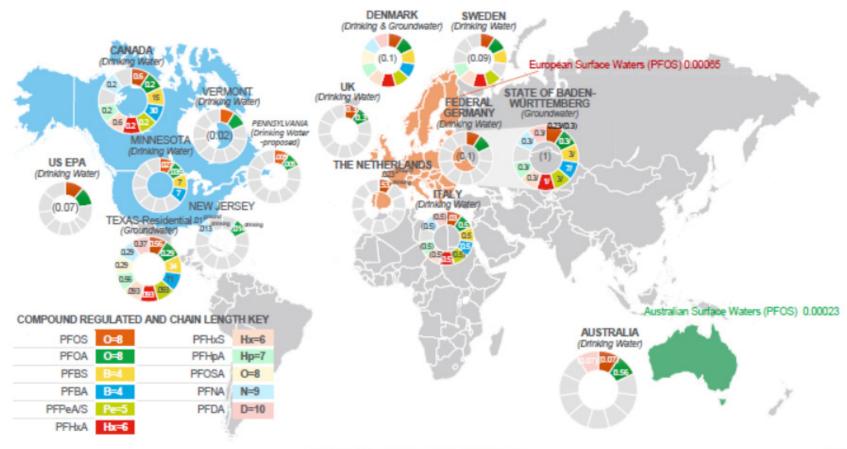
Global Regulatory Climate





Evolving Regulatory PFAS Values - Overview

Drinking, Surface and Ground Water (µg/l)



Analytical Challenges

- ☐ Low detection limits required
- ☐ Cross-contamination during sampling
- ☐ Deciding which analytes to quantify of the many that exist
- ☐ Standards not available for many analytes
- ☐ Fast-changing regulatory requirements and analytical methods



PFAS Analysis – "Standard" Method

Primary methodology

- Method 537 rev1.1 Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction (SPE) and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS), Sept,2009
- EPA Technical Advisory 815-B-16-021
 - PFAS compounds can exist as linear & branched isomers
 - Method 537 addresses both for PFOS but not PFOA
 - Discrepancies in PFOA analysis addressed in Tech Advisory
- Drinking water method
 - Amenable to a specific 14 cmpd PFAS target list

EPA Method 537 - List of 14 Compounds

Perfluorooctanoic	acid	(PFOA)
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Perfluorooctane Sulfonate (PFOS)

Perfluorobutanesulfonic acid (PFBS)

Perfluoroheptanoic acid (PFHpA)

Perfluorohexane Sulfonate (PFHxS)

Perfluorononanoic acid (PFNA)

Perfluorohexanoic acid (PFHxA)

Perfluorodecanoic acid (PFDA)

Perfluoroundecanoic acid (PFUdA)

N-methyl perfluorooctanesulfonamidoacetic acid (MeFOSAA)

Perfluorododecanoic acid (PFDoA)

N-ethyl perfluorooctanesulfonamidoacetic acid (EtFOSAA)

Perfluorotridecanoic acid (PRTrDA)

Perfluorotetradecanoic acid (PFTeDA)





Other LC/MS/MS Methodologies

- Method 537 not amenable to expanded list of compounds
 - 500 series DW methods not supposed to be modified
- "Laboratory proprietary methods" to address longer compound lists / sample matrices other than DW
 - Methods are developing fast





Fluoride and Total Organic Fluorine Analysis

- ☐ Fluoride analysis can be used to:
 - ➤ Evaluate extent of biological or chemical remediation that releases fluoride from PFAS
 - ➤ A drawback is high detection limits of ~20 ug/L
 - ➤ Drinking water standards/guidelines:
 - U.S. Public Health Service recommends 0.7 mg/L to prevent cavities
 - EPA MCL 4.0 mg/l and secondary MCL 2.0 mg/L
 - Concerns about thyroid, brain, and other impacts
- ☐ Total organic fluorine an emerging technique could be useful to:
 - ➤ Locate PFAS plumes
 - ➤ Verify remediation is complete



Transformation and Precursors

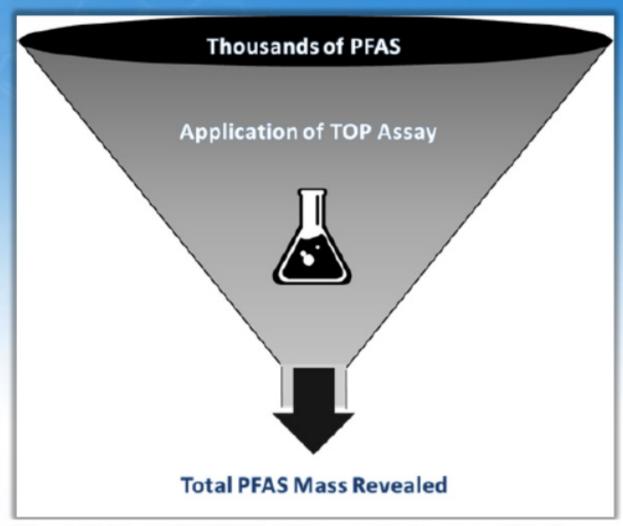
- ☐ Pers don't naturally transform
- Oxidizable polys should eventually transform to pers
 - ➤ Biotic or abiotic transformation
 - ➤ Polys cleave at a weak spot (i.e., a carbon not fully fluorinated)
- ☐ Total Oxidizable Precursors (TOP) analysis quantifies precursors to help assess the total mass and risk of PFAS



What is the TOP Assay?



- A new PFAS sample preparation technique
- Conceptually simple chemistry
- Used in conjunction with 537M (Not 537) – combines pre and post oxidation results
- Indicates presence of unidentified PFAS in water, sediment and soil



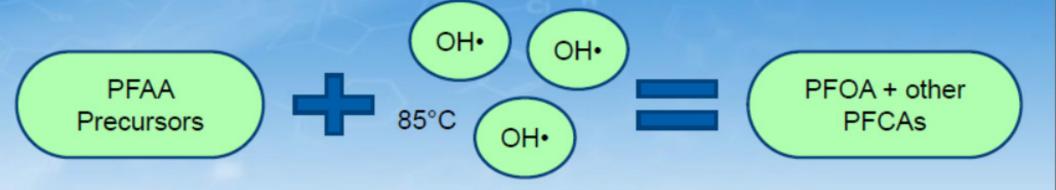


Houtz, Erika, and David L. Sedlak. 2012. Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff. *Environmental Science and Technology* 46: 9342-9349.

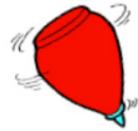
Image provided by Arcadis 2016

TOP – How Does it Work in the Laboratory?









Sampling - Possible Sources of Contamination

note: conflicting recommendations possible depending on source of information

OK

Field Equipment

 HDPE bottles, silicon tubing, loose paper, aluminum/masonite clipboards, nitrile gloves

Clothing / PPE

"Well laundered", preferably cotton

Personal care products

 see "allowable" sun screens & insect repellants

NOT OK

Field Equipment

 LDPE bottles, Teflon@ caps, Teflon@ tubing, waterproof field books, plastic clipboards/binders, Post It @ notes, chemical (blue ice)

Clothing / PPE

 No fabric softener, Gor-Tex[®], "dri -fit", Tyvek [®]

Personal care products

- No cosmetics, moisturizers, etc. as part of personal cleaning/showering routine on morning of sampling
- Verify allowable sun screens / insect
- Food packaging



References

- □ EPA. 2016. Health Advisories for PFOS and PFOA. https://www.epa.gov/ground-water-and-drinking-water-health-advisories-pfoa-and-pfos
- □ Environmental Working Group. 2017. Toxic Fluorinated Chemicals in Tap Water and at Industrial or Military Sites. http://www.ewg.org/interactive-maps/2017 pfa/index.php
- □ Kjølholt, J., Allan Jensen, and M. Warming. 2015 Short-chain Polyfluoroalkyl Substances (PFAS). A literature review of information on human health effects and environmental fate and effect aspects of short-chain PFAS:
 - https://www.researchgate.net/publication/299230070 Shortchain Polyfluoroalkyl Substances PFAS A literature review of information on human he alth effects and environmental fate and effect aspects of short-chain PFAS
- □ Buechler, Karla. 2017. The Analysis of Polyfluorinated Alkyl (PFAS) including PFOS and PFOA June 27, 2017. http://www.testamericainc.com/services-we-offer/webinars/presentations/presentation-the-analysis-of-polyfluorinated-alkyl-substances-pfas-including-pfos-and-pfoa/
- □ Buechler, Karla, 2017. Closing the PFAS Mass Balance: The Total Oxidizable Precursor (TOP)
 Assay May 15, 2017. http://www.testamericainc.com/services-we-offer/webinars/presentations/presentation-closing-the-pfas-mass-balance-the-total-oxidizable-precursor-top-assay/



Exercise: Properties, Uses, Occurrence and Concerns

- ☐ You've done an initial subsurface investigation of a PFAS release site and the client wants to clean it up
- ☐ Groundwater flows from the site toward an offsite drinking water well
- ☐ You analyzed groundwater samples for PFAS by Method 537M and detected PFOS and PFOA at concentrations 10 times state standards (no other PFAS were detected, nor were VOCs or other types of chemicals)
- ☐ What additional information would you target for the next round of investigation to determine the nature and extent of contamination?



PFAS Remedial Options for Source and Plume Areas



Physical-Chemical Properties

Property	PFOA	PFOS	Benzene				
Chemical Formula	$C_8HF_{15}O_2$	$C_8HF_{17}O_3S$	C_6H_6				
Molecular Weight (g/mol)	414.09	500.13	78.11				
Boiling Point (°C)	192.4	259	80				
Vapor Pressure (mm Hg at 25 °C)	0.525	~0.002	86				
Henry's Law Constant @ 25°C (unitless)	Not measurable	Not measurable	0.225				
K _{oc} (temperature as specified)	115	371	79 (at 25 °C)				
Solubility in Water (mg/L)	~9,500 (at 25 °C)	680 (temp. not stated)	1,780 (at 25 °C)				
	USEPA 2016	USEPA 2016					



Overview

- ☐ Based on the physical/chemical properties of PFAS (the higher C PFAS)
 - ➤ High molecular weight = potential for sieving / filtration
 - ➤ High Koc = potential for adsorption
 - ➤ Charged group = potential for ion exchange
 - ➤ Low VP = not suitable for SVE at ambient temperatures
 - ➤ Low H = not suitable for stripping from groundwater at ambient temperatures
- ☐ Biodegradation
 - ➤ Very limited research to date showing biodegradation of Pers
 - No accumulation of byproducts or Fluoride in studies raises questions
 - Evidence of transformations of Polys
 - Question on whether can treat to the proposed standards
 - Mother nature will likely find a way to degrade Pers with time?
- Oxidative / reductive technologies
 - > Showing promise, but some unanswered questions
 - > Common theme is high energy and / or diverse reactive species needed
- Thermal how hot?



Remedial Technologies with "Success" in PFAS Treatment

(Success may have been only achieved at bench-scale level)

- ☐ Physical treatment/removal
 - ➤ Filtration/reverse osmosis*
 - ➤ Adsorption/ion exchange (IX)*
 - Excavation + disposal / isolation
 - ➤ In-situ stabilization
- ☐ Chemical Oxidation / Reduction
 - Various high energy oxidant / reductant systems
 - Sonolysis
 - > Photolysis

- ☐ Biotransformation
 - > Partial?
 - Not for C-F bond?
- ☐ "Other"
 - Destruction at high temperature > 1,100 °C
 - Pyrolysis
 - Can "enhance removal" at lower temperatures e.g., thermal desorption
 - Electro-chemical / catalytic

^{*} Typically associated with ex-situ treatment



Summary of Ex-Situ Water Treatment Options Evaluated

Compound	Acronym	Molecular Weight (g/mole)	Aeration	Coagulation Dissolved Air Floatation	Coagulation Flocculation Sedimentation Filtration	Conventional Oxidation (MnO ₄ , O ₂ , ClO ₂ , CLM, UV-AOP)	Anion Exchange (Select Resins Tested)	Granular Activated Carbon	Nano Filtration	Reverse Osmosis
Perfluorobutanesulfonic Acid	PFBS	300								
Perfluoroheptanoic Acid	PFHpA	364								1
Perfluorohexanesulfonic Acid	PFHxS	400								
Perfluorooctanoic Acid	PFOA	414								
Perfluorononanoic Acid	PFNA	464		unknown			assumed	assumed		
Perfluorooctane Sulfonate	PFOS	500								
							Table mod	lified from E. D	ickenson and C	. Higgins 2016
		> 90% removal			>10%, < 90% removal		< 10% removal		ı	

E. Dickenson and C. Higgins, "Treatment Mitigation Strategies for Poly- and Perfluoroalkyl Substances," Water Research Foundation, 2016.



Filtration

Essentially "Sieving" of PFAS molecules

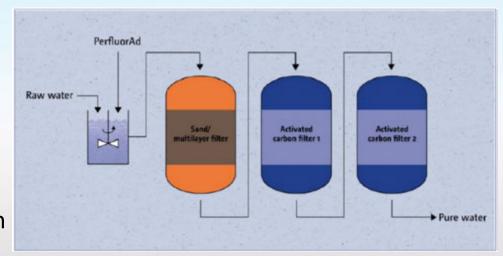
- ☐ Nano-Filtration (NF)
 - > PFAS have molecular weight cutoff (MWCO) of approximately 300 500 Daltons
 - Measure of size restriction to pass through filter media
 - ➤ NF MWCO > 200 Daltons, therefore >90% effective most PFAS
 - Ultra and micro-filtration low effectiveness
- ☐ Reverse Osmosis
 - ➤ Polymers used have spaces on the order of 100 200 Daltons
 - > >90% effective most PFAS
- ☐ Concentrated waste streams result / require treatment
 - Typically incineration at > 1100 oC
- ☐ PerfluorAd not really filtration but pretreatment



PerfluorAd Principle of Operation

For every zone of your plume, we've got you covered!

- Added to PFASs contaminated water in stirring reactor
- Dosing rate adjustable to PFASs concentration or target
- Micro-flocs are generated
- Flocs removable by precipitation & filtration
- 95%+ PFASs removal attainable
- Non-detect concentrations with GAC/PAC polishing





Adsorption/Ion Exchange (most commonplace)

- ☐ Carbon-based systems
 - > Ex-situ activated carbon systems (granular [GAC] or powered [PAC])
 - ➤ In-situ injectable carbon-based systems
 - Questions exist on design / long term performance
- ☐ Clays or blend of sorbent-based systems
 - ► e.g., RembindTM, MatCARETM
 - > Part isolation?
- ☐ Synthetics resins gaining traction due to capacity/effectiveness
 - Combination IX and adsorption
- ☐ Zeolites? in R&D

Treatability studies are essential



GAC / PAC Proven Technology

- ☐ Not all GAC are created equal
 - Carbon source and manufacturing can impact capacity and effectiveness
- ☐ GAC has been used for more than 15 years in over 30 large installations for both drinking water and PFAS remediation applications (also for POET)
- ☐ Spent GAC containing adsorbed PFAS can be recycled
 - > PFAS are thermally destroyed







Research Study

Comparison of Various GAC for PFOA and PFOS Removal

☐ Four GAC products evaluated under identical operating conditions and influent water quality

Carbon	Description		
Filtrasorb – Virgin	Bituminous Reagglomerated Coal 12x40 mesh		
Coconut 8x30	Direct activated Coconut 8x30 mesh		
Coconut 12x40	Direct activated Coconut 12x40 mesh		
Filtrasorb – React	Reactivated Bituminous Reagglomerated Coal 12x40 mesh		

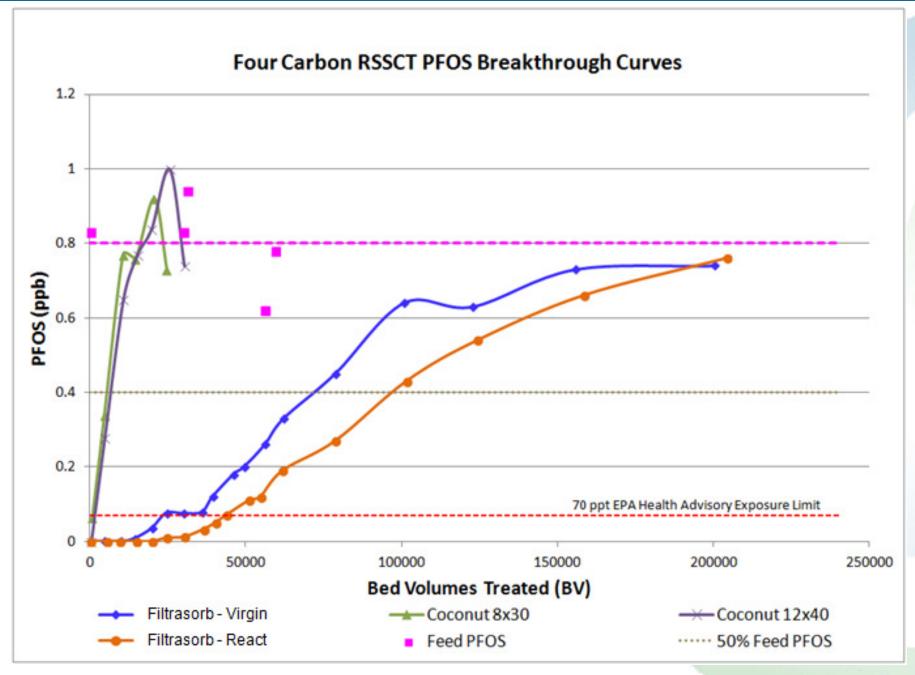


GAC Comparison Test Conditions

Operating Parameters

- □ 10 minutes empty bed contact time (EBCT)
- □Center Township, PA groundwater
 - > Water did not have PFCs as received
 - ➤ Water was spiked to contain:
 - 920 ppt of PFOA (target 1,000 ppt)
 - 800 ppt of PFOS (target 1,000 ppt)
 - ► 1.42 ppm background TOC





© Calgon Carbon Corporation, 2017



Treatability Studies are Critical

Why

☐ Many factors influence the effective service life of GAC

- **≻**Temperature
- ≽pH
- **≻**EBCT
- **≻**Concentration
- **≻**Competitive Adsorption
- □Extremely difficult to quantify without testing

Objectives

□Application Research

- ➤ Best GAC for the application
- ➤ Design recommendations

□Customer Specific

- **≻**Feasibility
- ➤ Exchange frequency

Methods

☐ Isotherm Testing

- > Feasibility adsorption of the target contaminants
- ➤ Quick comparison of performance of various carbon types
- >Impacts of changeable operating parameters on the adsorbability of target contaminants

□Column Testing (ACT or RSSCT)

- > Define the kinetics of adsorption or minimum contact time required
- ➤ Define accurate carbon use rates impacted by competitive adsorbing compounds



Treatment Methodology

Dual vessel treatment

☐ Maximize carbon loading

☐Simplifies carbon exchange logistics

□ Redundancy

Sufficient contact time is critical to effective removal

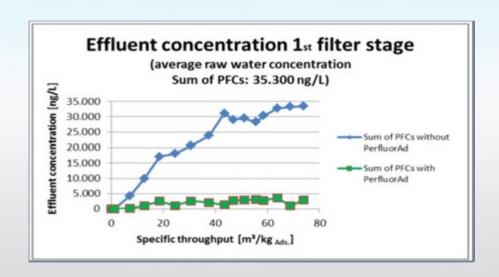
□Adsorption of PFCs by GAC is kinetically driven

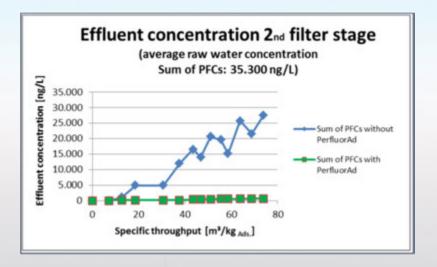
□ 10 minutes EBCT per vessel minimum



Treatment with / without PerfluorAd

For every zone of your plume, we've got you covered!





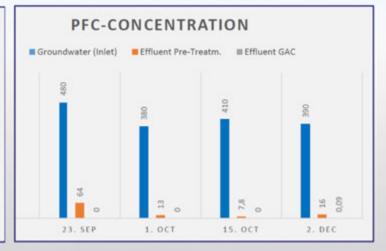


Nuremburg PerfluorAd Performance Results

For every zone of your plume, we've got you covered!

PFASs Treatment

Sampling Date	Groundwater (Inlet)	Effluent Pre-Treatm.	Effluent GAC	Removal PerfluorAd
23. Sep	480	64	0	86,7
1. Oct	380	13	0	96,4
15. Oct	410	7,8	0	98,1
2. Dec	390	16	0,09	95,9





In-situ vs. Ex-situ Treatment of PFAS

(Questions to think about)

☐ In-situ advantages:

- ➤ Potential lower capital and O&M costs
- ➤ Less infrastructure aboveground

☐ Ex-situ advantages:

- ➤ Hydraulic containment
- ➤ More ways to measure and control the process
 - Easier to replace remediation materials in vessels than subsurface
 - Avoid potential of recontamination (e.g., adsorbent life and competition for sorption sites)
 - Less sensitivity to unknown contaminant mass
- Can put multiple treatment vessels in series to detect and deal with breakthrough from the first vessel
- ➤ Reduce risk of clogging the formation



In-Situ Injectable Carbon-Based Systems

(e.g., Plume Stop, BOS)



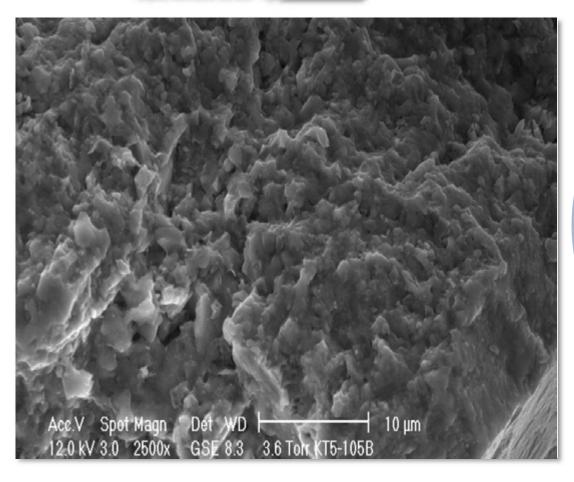
- A highly dispersive, injectable sorbent and microbial growth matrix
- Colloidal activated carbon $(1 2 \mu m)$
 - Size of a bacterium suspends as 'liquid'
 - ➤ Huge surface area extremely fast sorption
- Proprietary anti-clumping / distribution supporting surface treatment (patent applied for)
 - > Core innovation
 - Enables wide-area, low-pressure distribution through the soil matrix without clogging

Courtesy Regenesis





PLUME STOP Mode of Action - PFAS



Sorption sites
become available
for additional
contaminant

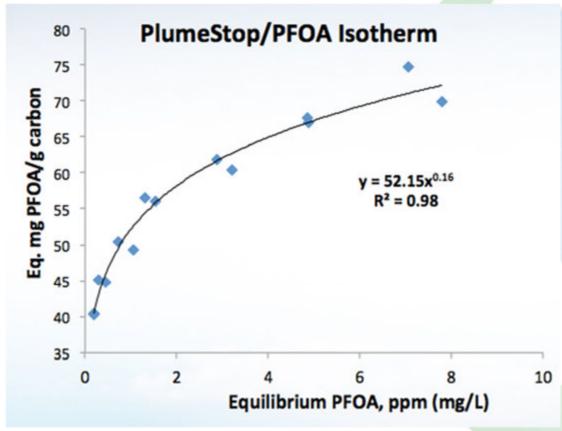
Microbes
biodegrade
sorbed
contaminants

Courtesy Regenesis

? Added







Sorption only (currently no validated destruction methods are available)

Courtesy Regenesis



What is RemBind®?



For every zone of your plume, we've got you covered!

- Powdered reagent that binds to organic contaminants in soil/water to prevent leaching
- Chemical fixation or immobilization
- Binds to range of contaminants including TPH, PAH, and PFASs
- US Patent 8,940,958





How Does RemBind® Work?



For every zone of your plume, we've got you covered!

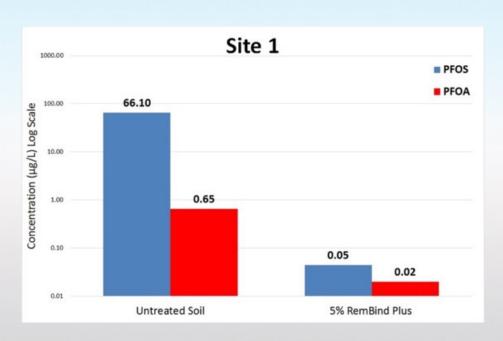
- Main ingredients:
 - Activated carbon
 - Aluminium hydroxide (amorphous)
 - Organic matter and additives
- Large surface area with mixed charges
- Chemical and physical interactions



PFOS and PFOA Soil Results



For every zone of your plume, we've got you covered!





* Soil leachates prepared using the Toxicity Characteristic Leaching Procedure (TCLP)

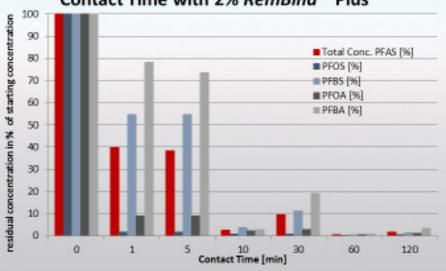




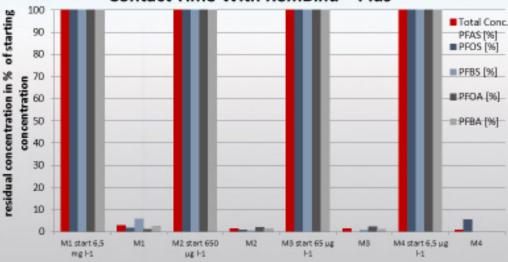
Using RemBind® to remove short- and longchain PFAS from water

2% RemBind™ Plus





Residual PFAS Concentration After 60 Minute Contact Time With RemBind™ Plus





Resins

☐ Synthetic Media can be engineered / used to collect various contaminants from liquids, vapor or atmospheric streams and be reused indefinitely











Bench-Scale Column Testing of four IX Resins







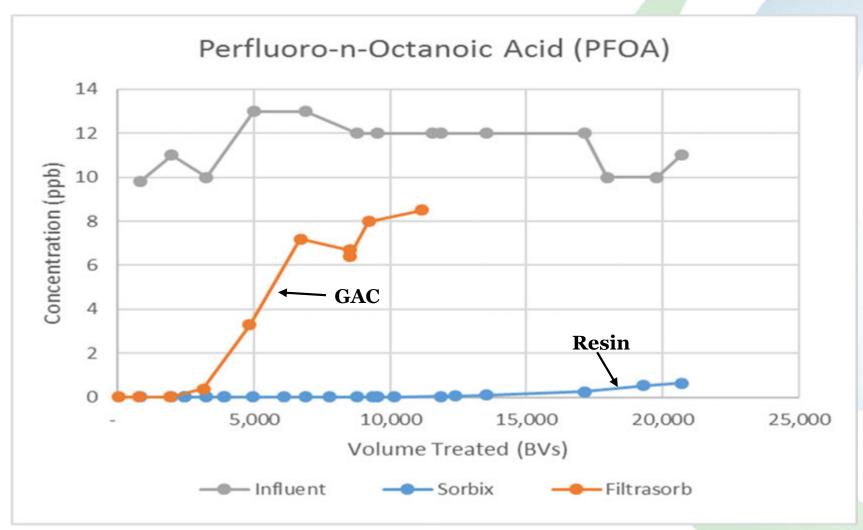
Overview Sorbix

- ☐ Sorbix is essentially an adsorbent with IX functionality
- Dual mechanism of removal takes advantage of properties of PFAS compounds
- □ Capacity is 5-6X greater than GAC for PFOA and > 8X greater for PFOS.
- ☐ Successful resin regeneration has been demonstrated
- ☐ Distillation and PFAS destruction maximize sustainability
- ☐ New resins are being tested: i.e., removal of shorter chain compounds





PFOA Breakthrough at 5-min EBCT

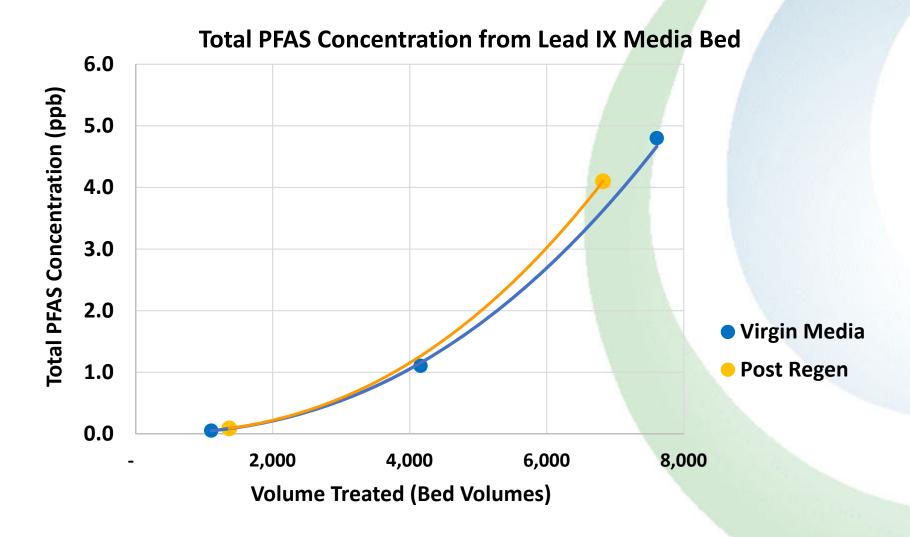


BV = bed volumes EBCT = empty bed contact times





Regeneration of IX Resin at Pilot Scale







Carbon vs. IX Resins

- Carbon
 - > Proven effective multiple sites and >1000 point of entry treatment systems
 - Regeneration, at high temperature: "destroys" PFAS but may reduce capacity
 - ➤ Lower capacity than IX
 - > Still evaluating short chain PFAS, but some success
 - Can be more cost-effective
 - If shorter duration operations, lower PFAS concentrations, and less natural organic matter
- Resins
 - Number case studies increasing
 - ➤ Higher capacity for PFAS adsorption / IX
 - Working on engineering resins for improving short chain PFAS removal
 - > Can be more cost-effective
 - > On-site regeneration and PFAS destruction research/demonstration ongoing
- ☐ Treatability studies are essential for design, etc.



Chemical Oxidation / Reduction In Situ or Ex Situ

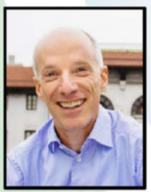
- ☐ Several bench studies / few pilots performed over last several years showing partial to full destruction of PFAS
 - Focus has typically been on PFOA and PFOS
- ☐ Common theme observed in chemical approaches is success when creating complex chemistries / radical mixtures
 - Creating reductive and oxidative radicals
- □ Also success under high temperature / pressure conditions practical?
 - > e.g. high temperature permanganate; high temperature and pressure ZVI
- ☐ Research ongoing using chemical oxidation to treat precursors to simplify overall treatment approach



Pretreatment of Precursors

Fighting the Unbeatable Foe: Remediation of Groundwater Contaminated by PFASs with In Situ Chemical Oxidation

Dr. David Sedlak University of California, Berkeley

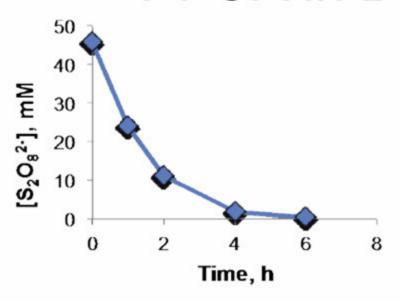


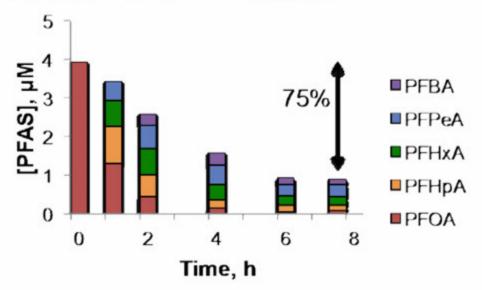






PFOA in Deionized Water

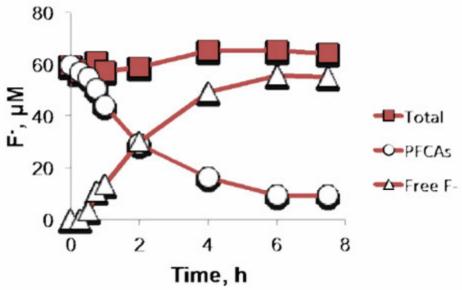




Conditions:

 $[S_2O_8^{2-}]_0 = 50 \text{ mM},$ $[PFOA]_0 = 4 \mu\text{M}$ unbuffered (pH < 3) H₂O, $T = 85^{\circ}\text{ C}$

Bruton and Sedlak, in review



SERDP & ESTCP Webinar Series (#59)

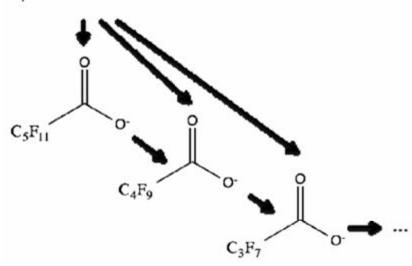


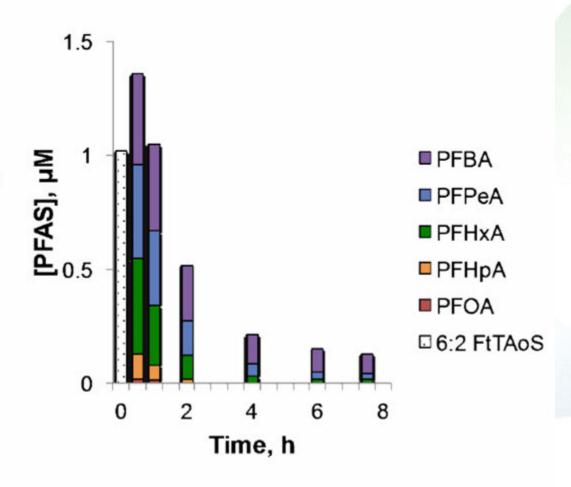
Ansul AFFF

Conditions:

$$[S_2O_8^{2-}]_0 = 50 \text{ mM},$$

unbuffered (pH < 3) MQ H₂O,
T = 85° C





SERDP & ESTCP Webinar Series (#59)

Bruton and Sedlak, in review

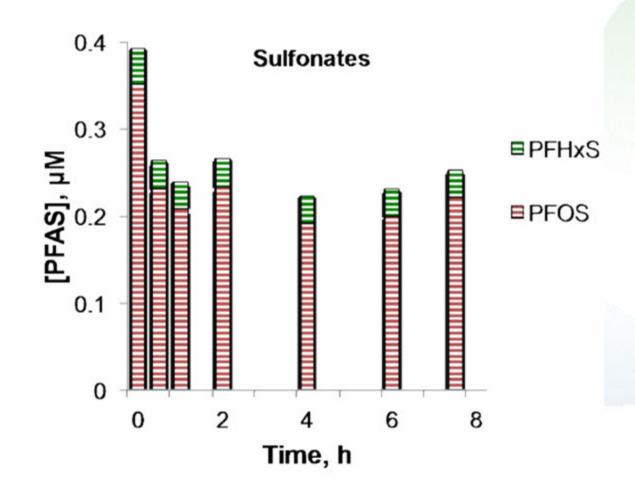
61



3M AFFF: Sulfonates

Conditions:

 $[S_2O_8^{2-}]_0 = 50 \text{ mM},$ unbuffered (pH < 3) MQ H₂O T = 85° C



SERDP & ESTCP Webinar Series (#59)

Bruton and Sedlak, in review



Summary

- Persulfate or H₂O₂ ISCO can convert polyfluorinated compounds into PFCAs
 - Complex AFFF "precursors" converted to PFCAs
 - Benefit: simplifies remediation process
- Persulfate mineralizes PFCAs
 - Only under acidic conditions (pH<3)
 - Interference from chloride
 - Benefit: in situ remediation of PFCAs and Ansul AFFF
- Limitations
 - PFSAs, 3M AFFF, high alkalinity, Cl-

SERDP & ESTCP Webinar Series (#59)



Exercise: PFAS Remedial Options

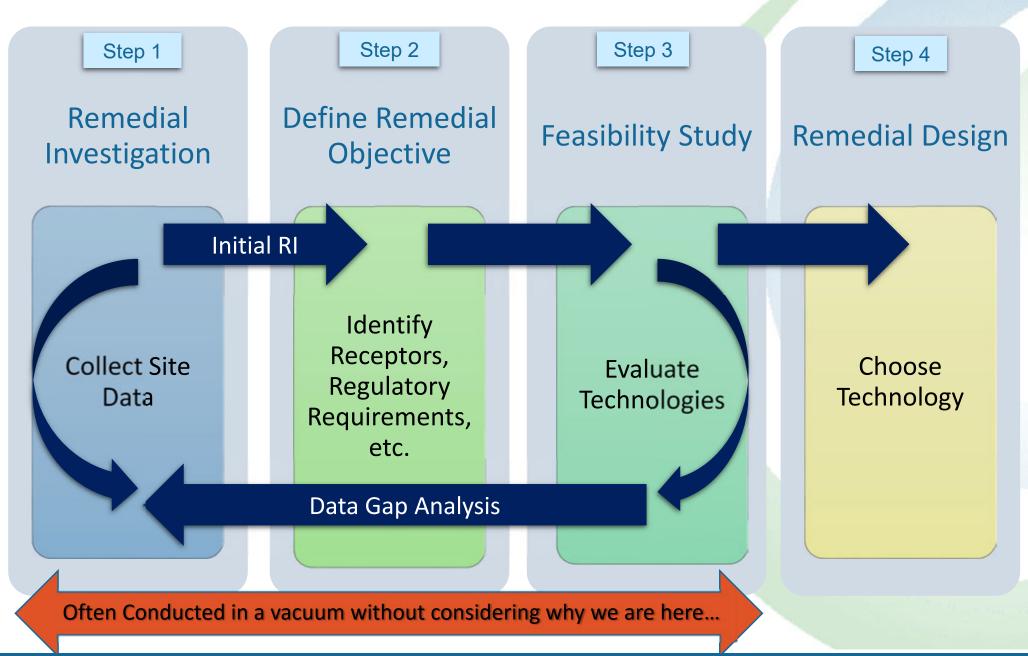
☐ For the same site above, contaminated source area soil has been excavated and disposed of offsite, and a new water well was drilled for the drinking water user. Additional groundwater testing indicates the presence of significant concentrations of precursors. 1) What would be some good remedial options to consider for the site groundwater containing PFOS, PFOA, and precursors? 2) What questions should we be asking as we consider remedial options?



Integrating Key Data Collection into Characterization



Old Thinking: RI/FS → Remedial Design



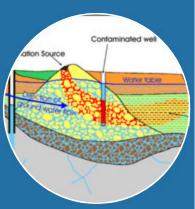


New Thinking: Integrated Remedial Strategy



Define Objective

- Sensitivity of receptors, applicable regulations, etc.
- Site Closure



Define Criteria

- Set reasonable criteria to achieve goals
- Incorporate nonremediation approaches (risk, assessment, etc.)



Remedial Investigation

- Focus RI to get data that supports goal
- Actively screen remedial options during process



Feasibility Study

 Collect field data to support design, bench, pilot study



Remedial Design

 Choosing technology (or hybrids) to meet goals with higher confidence

Sights set on closure from beginning of RI/FS through all phases



Some of Issues / Options for Site Characterization

- ☐ Reminder on issues
 - ➤ Limitations of PFAS laboratory analyses
 - > We don't understand the risk associated with every PFAS
 - ➤ We don't understand the physical chemical properties of every PFAS
 - ➤ Focus on PFOA and PFOS may be forefront today, but.....
- ☐ General Parameters
 - **>** Geology
 - > Hydraulics
 - ➤ All contaminants of concern (source and plume)
 - ➤ Receptors
 - > Remedial goals
 - ➤ Logistical issues (e.g. access)
 - ➤ Geochemistry general (including DO, ORP, pH)
 - ➤ Geochemistry technology specific (including alkalinity, metals, major anions and cations)?



Some of Issues / Options for Site Characterization

- ☐ To understand degree of PFAS impacts (i.e., not just PFOA and PFOS)
 - ➤ TOP analysis
 - ➤ Emerging analysis TOF
 - > Free Fluoride evidence of transformation?
- ☐ Source Treatment
 - **Excavation**
 - What is the cut-off concentration / limit for excavation?
 - ➤ Isolation / Stabilization
 - Compatibility with isolation materials
 - Treatability study on leachability of stabilized soils TCLP?
 - > In-situ chemical treatment
 - Treatability study on effectiveness, byproduct formation, chemical loading (includes non-target demand), remedial goal achievable?
 - ➤ In-situ adsorption
 - Treatability study on amendment loading, effectiveness for all PFAS, leachability of sorbents and competitive adsorption species (e.g. TOC)



Some of Issues / Options for Site Characterization

☐ Plume Treatment

≻Containment

- Pump and Treat
 - Sorbents treatability study on effectiveness all PFAS of concern, EBCT, breakthrough, remedial goal achievable
 - Filtration treatability study on effectiveness all PFAS of concern, system sizing, remedial goal achievable
 - o Chemical treatment treatability study on effectiveness all PFAS of concern, byproduct formation, chemical loading, EBCT, remedial goal achievable
- Barrier systems
 - o Sorbents treatability study on effectiveness all PFAS of concern, loading, breakthrough, remedial goal achievable
 - o Chemical treatment treatability study on effectiveness all PFAS of concern, byproduct formation, chemical loading, breakthrough, remedial goal achievable



Some of Issues / Options for Site Characterization

☐ Plume Treatment

- ➤ In-situ chemical treatment
 - Treatability study on effectiveness for all PFAS, byproduct formation, chemical loading, remedial goal achievable, aquifer clogging potential (e.g., mineral precipitation)
- ➤In-situ adsorption
 - Treatability study on material loading, effectiveness for all PFAS, leachability of sorbents and competitive adsorption species (e.g. DOM), aquifer clogging potential (e.g., mineral precipitation)



Exercise: Integrating Key Data Collection into Site Characterization

☐ What analyses do you wish you had included in the additional testing that would help determine the optimal remedial approach for site groundwater?



Exercise: Treatability Studies

☐ We've identified some potential remedial options for site groundwater that look promising. And we've filled the data gaps identified in the last exercise. What questions could treatability testing answer about remediating the site GW?



Adsorption Case Studies



Comparison of Various GAC for PFAS Removal

☐ Multiple PFAS, variety of chain lengths

Each compounds spiked to approximately 200 ppt

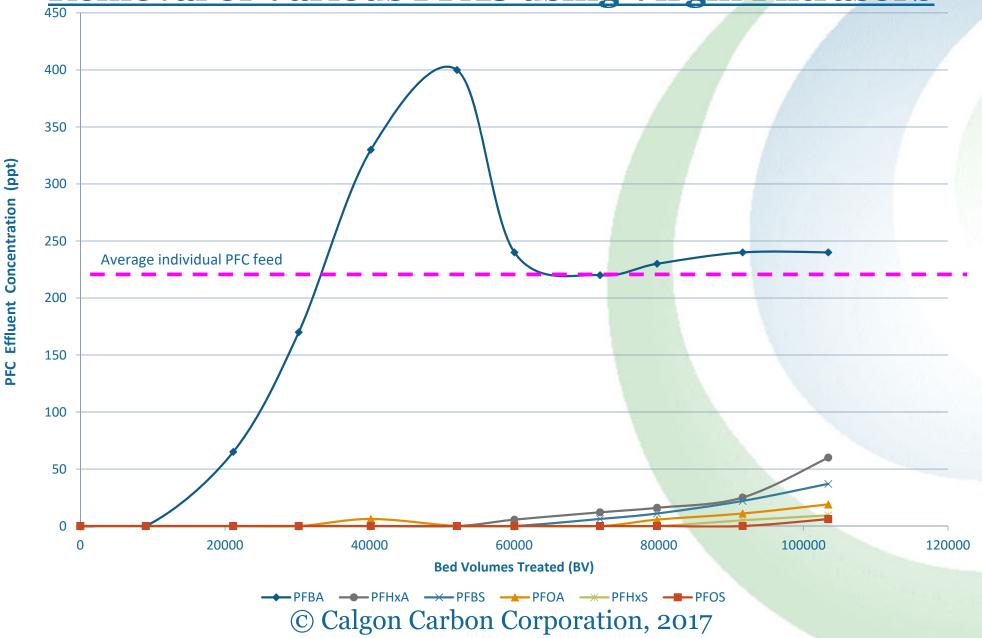
Name	Abbreviation	CAS Number	Carbon Chain Length	Molecular Weight (g/mol)
Perfluoro octanesulfonic acid	PFOS	1763-23-1	C8	500.13
Perfluoro octanioc acid	PFOA	335-67-1	C8	414.07
Perfluorohexanesulfonic acid	PFHxS	355-46-4	C6	400.11
Perfluoro hexanoic acid	PFHxA	307-24-4	C6	314.05
Perfluoro butanesulfonic acid	PFBS	375-73-5	C4	300.1
Perfluoro butanoic acid	PFBA	375-22-4	C4	214.04

- ☐ Background TOC 0.16 ppm
- ☐ Simulated EBCT 10 minutes



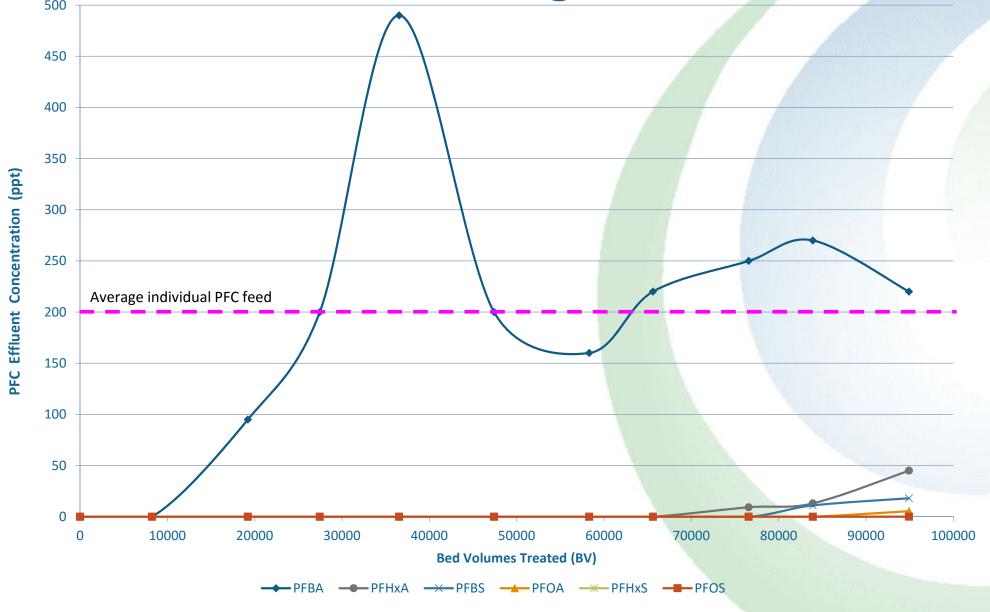


Removal of Various PFAS using Virgin Filtrasorb





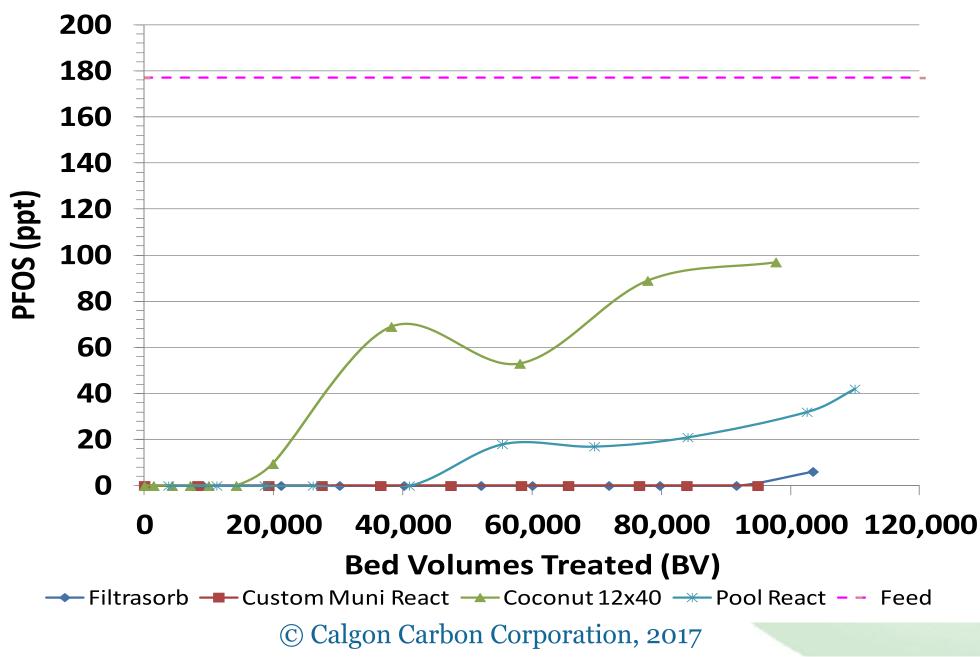
Removal of Various PFAS using Reactivated Filtrasorb



© Calgon Carbon Corporation, 2017



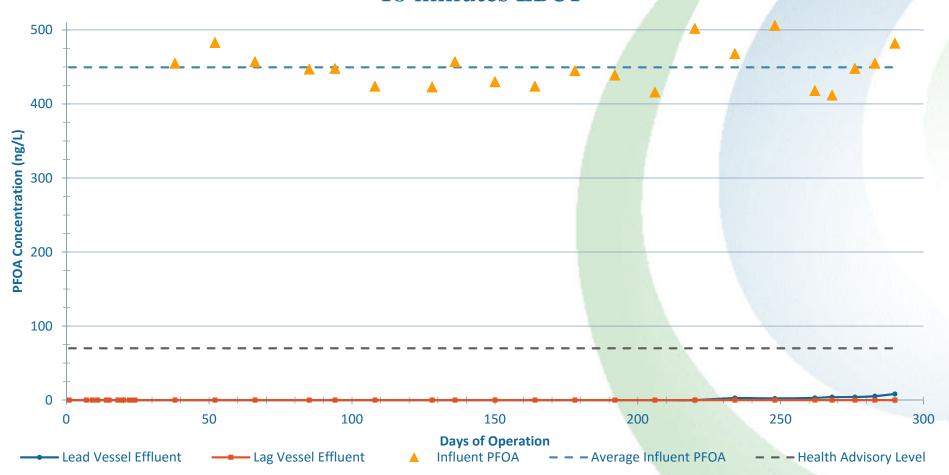
PFOS Breakthrough Comparison, EBCT 10 Minutes





Customer Field Data

Temporary Model 10 System 10 minutes EBCT



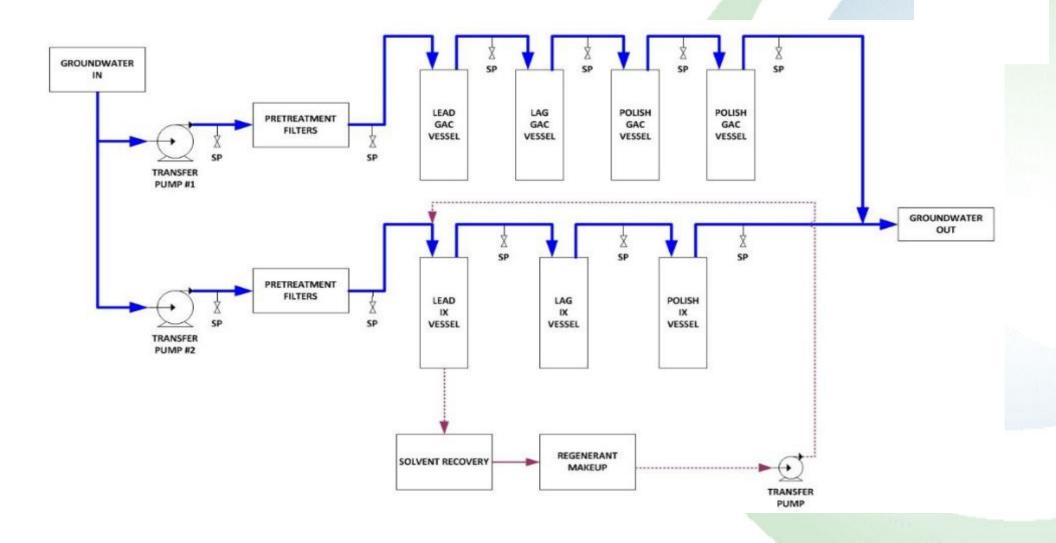
© Calgon Carbon Corporation, 2017







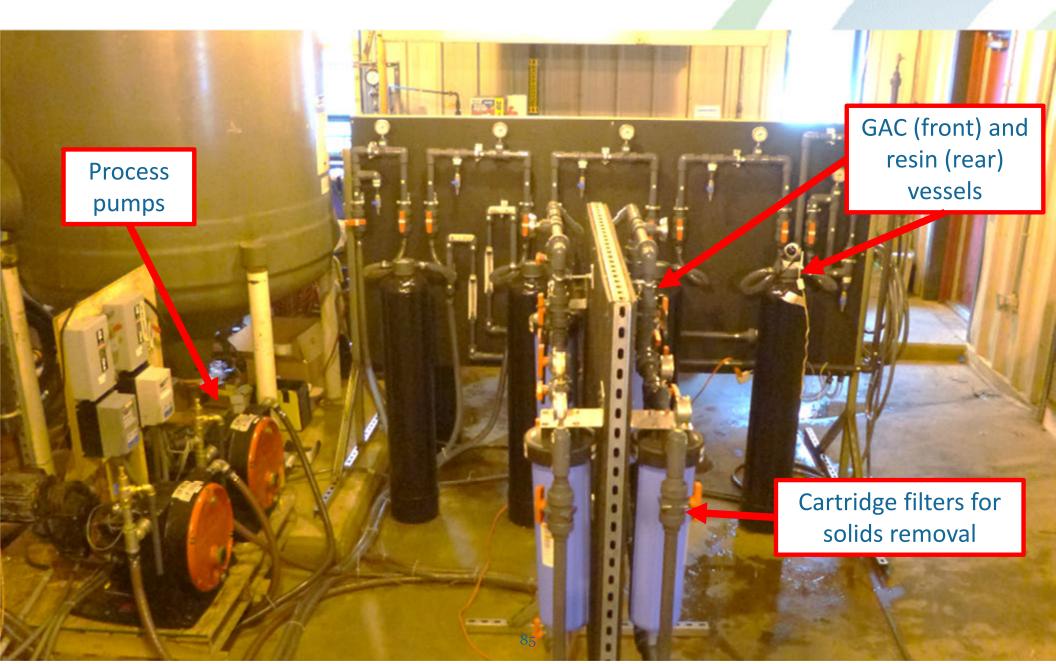
Pilot Test Process Flow Diagram



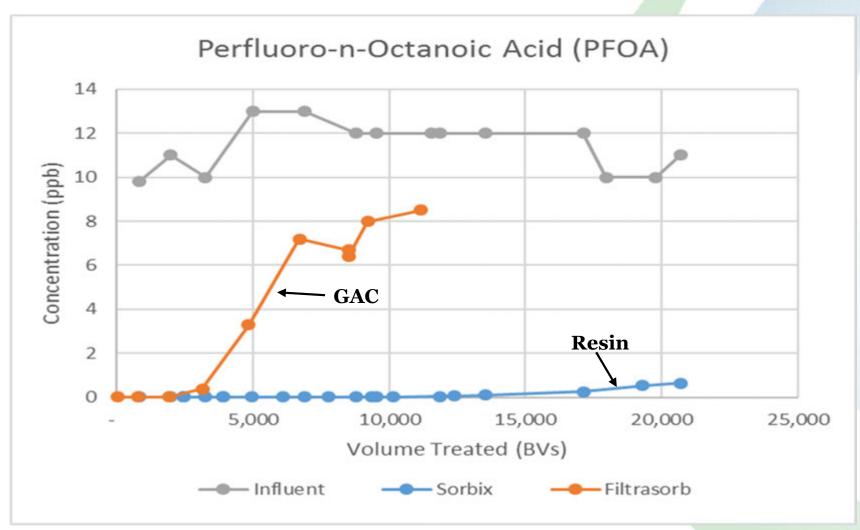
Pilot Test: IX Resin vs. GAC







PFOA Breakthrough at 5-min EBCT

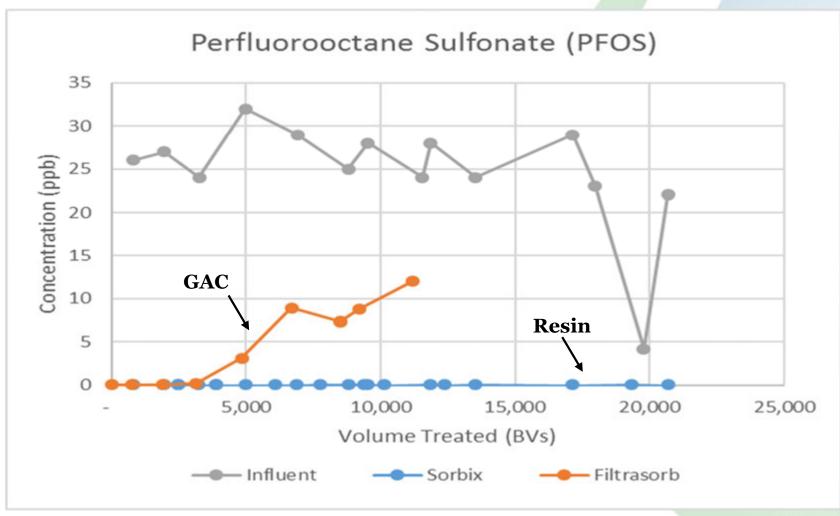


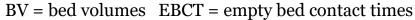
BV = bed volumes EBCT = empty bed contact times





PFOS Breakthrough at 5-min EBCT

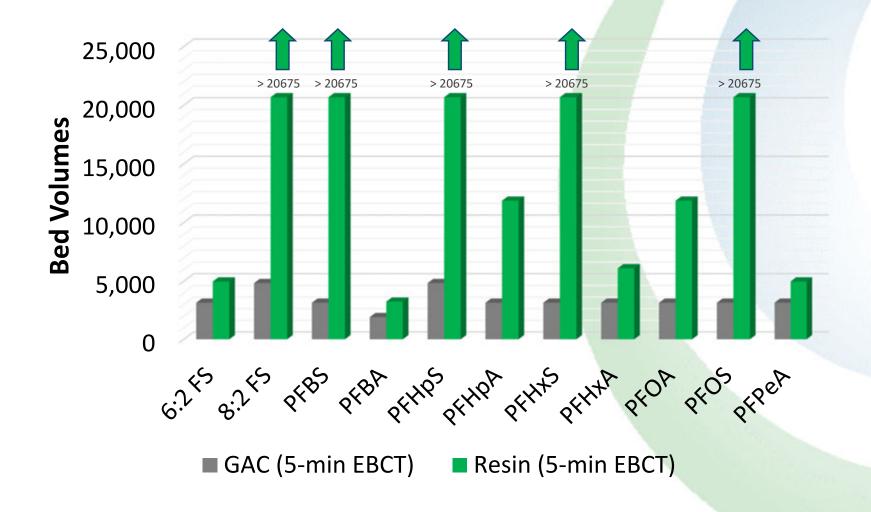








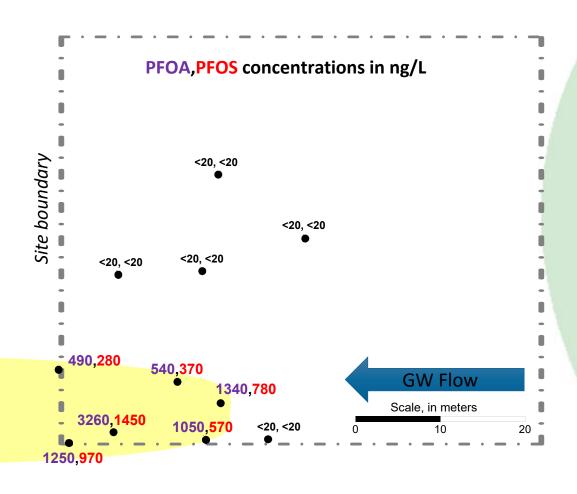
Volume Treated Before Breakthrough







Regenesis Case Study - PLUME STOP



Location: Canada

Soil:

Silty sand

DTW: 4 ft

GW velocity: 2 ft/day

History:

- Hydrocarbon spill
- Former fire training area

Baseline Contamination:

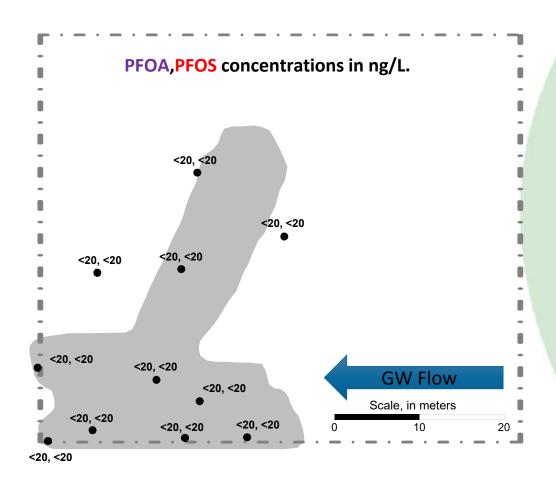
PFOS: $0.3 - 1.5 \mu g/L$ PFOA: $0.5 - 3.3 \mu g/L$

BTEX: $< 0.5 - 264 \mu g/L$

TPH: $<25 - 6,000 \mu g/L$



Regenesis Case Study



Remedial Technology Used:



Results

PFOS: ND (<20 ng/L)

PFOA: ND (<20 ng/L)

BTEX: ND ($<0.5 \mu g/L$)

TPH: ND (<25 μg/L)

Through 3, 6, and 15month (May '17) monitoring events



Exercise: In-Situ Adsorption

☐ What additional data collection or analyses do you wish too include to help determine if this is the optimal remedial approach for site groundwater?



Chemical Oxidation Case Study

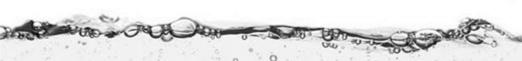








OxyZone® Chemistry



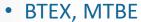
- Patented persulfate-based oxidant mixture
- Safe to apply under buildings
- Small site footprint, generation entirely enclosed
- Requires fresh water source and electrical hookup
- Equipment designed and built in-house
- Proven to be effective for in-situ treatment of conventional and emerging organic contaminants





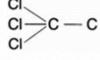
OxyZone®: Contaminants Treated

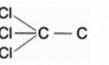
- Gasoline, diesel fuel oil spills:
 - Petroleum hydrocarbons (e.g. BTEX, gasoline, fuel oil) including achieving GW-1 drinking water standards)



- Polynuclear aromatic hydrocarbons (PAH)
- Dry Cleaners and other chlorinated VOCs

- Emerging Contaminants
 - 1,4-Dioxane
 - Perfluorooctanesulfonic Acid (PFOS), PFOA and other fluorinateds



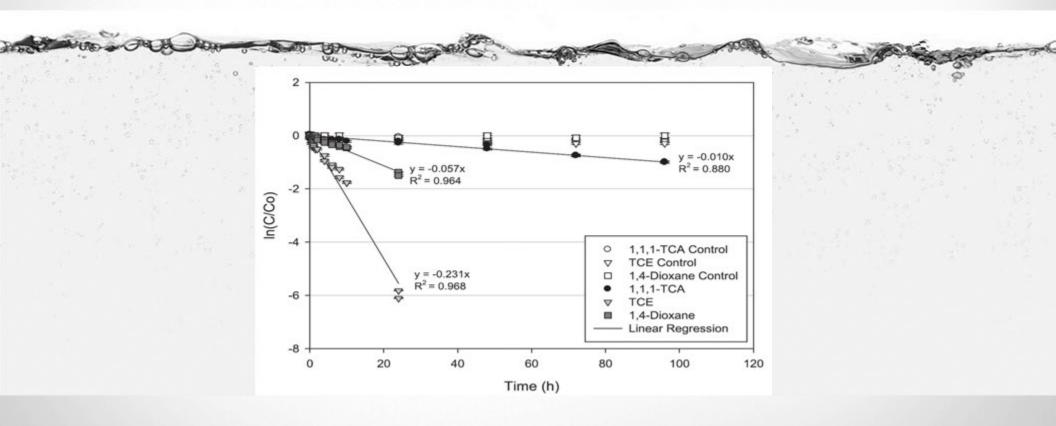






OxyZone® Treatability Test Results

Degradation of TCE; 1,1,1-TCA and 1,4-dioxane by OxyZone®, with Controls





Field Demonstration Test of Mixed Organics Remediation

EnChem Engineering

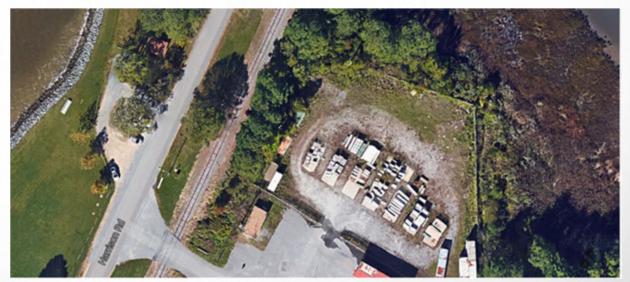
Summary

- Fire Training Area (FTA) at Joint Base Langley-Eustis (JBLE) in Hampton, VA
- Mixed organic wastes released and contaminated soil and GW
- 9 Month Field Demonstration
- OxyZone® Injection test cell of 20 feet by 30 feet
- Successful aromatic and chlorinated VOC treatment
- Groundwater PFAS Results showed statistically significant reduction
- PFAS destruction confirmed by laboratory bench scale testing



Field Demonstration

- ▶ Historical military FTA where Aqueous Film-Forming Foam (AFFF) released
- Complex geology, shallow GW (1-2'), low GW velocity, tidal influenced
- ▶ Surficial (shallow and intermediate) aquifer underlain by a clay confining unit
- ► Shallow (2-10' bg) silty sands and organic silt (K=0.5 m/d)
- Intermediate (10-20' bg) Highly permeable poorly sorted sands (K=4.9 m/d)





Field Demonstration – Subsurface Conditions

- Highest groundwater VOC concentrations were localized in some areas of the shallow zone.
- The highest VOC concentrations in deep groundwater were located directly below and down-gradient of the shallow source zone.
 - Mix of contaminants in site soil & GW at very high concentrations (NAPL)

◦ Chlorinated solvents (PCE, 1,1,1-TCA, DCB):
 10 – 250 mg/l (total)

Total Petroleum hydrocarbons (BTEX):
 0.1 − 5 mg/l

o Total SVOCs (mostly phenolics):
 0.5 − 50 mg/l

∘ Total of 9 detected PFAS: 28 − 280 ug/l

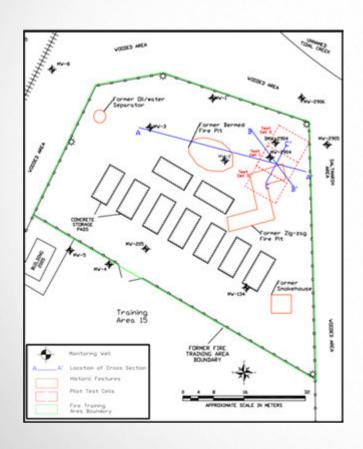
∘ PFOS (the dominant PFAS): 7 − 200 ug/l

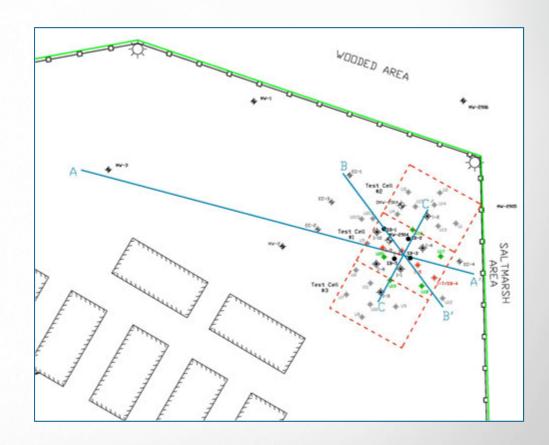
PFOS also dominant PFAS in soil: 1-150 ppb

* CoCs with highest concentrations



Field Demonstration – Test Cells

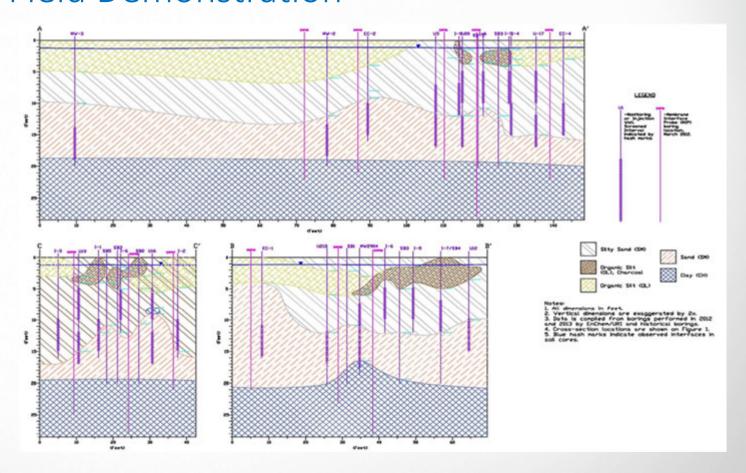






Field Demonstration

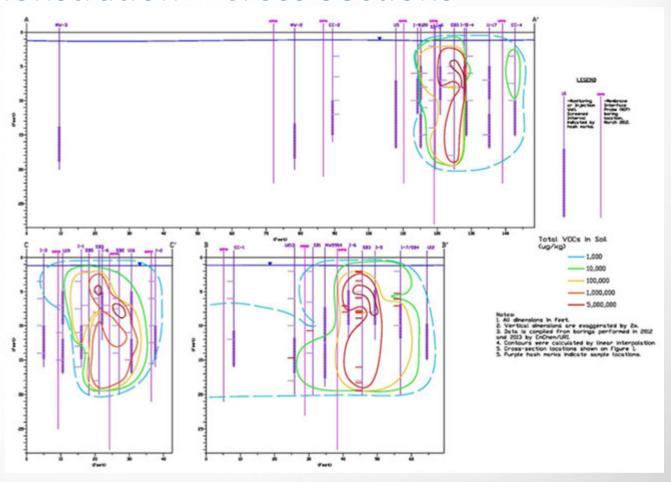
Geologic Cross-Sections





Field Demonstration – Cross Sections

Contamination Cross-Sections





Field Demonstration

Study Approach

- Pre-injection MIP and soil investigation to fully define extent of VOC and SVOC contamination.
- Pre-injection bench testing of NAPL treatment
- Pre-injection PFAS soil and groundwater analysis
- Three XCT[™] and OxyZone[®] injection events completed in the Test Cell at the site
- Post injection soil and groundwater (2x) sampling, including PFAS
- Laboratory OxyZone® tests to confirm PFAS treatment

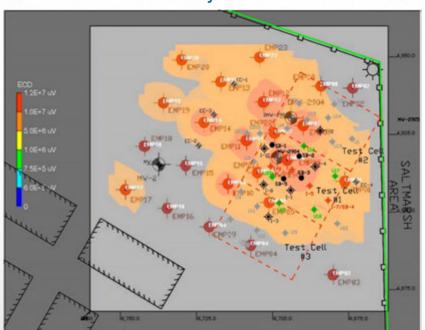




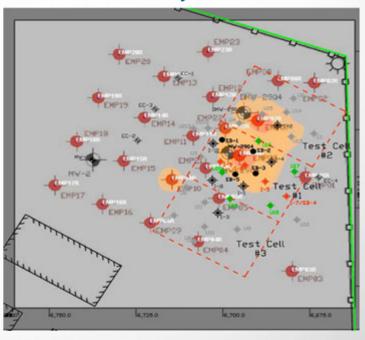
Field Demonstration Results for Chlorinated VOCs using Membrane Interface Probe (MIPs):

- Significant overall reduction in Chlorinated VOCs
- PFAS concentrations too low to be detected by MIPS

Pre-injection



Post-injection

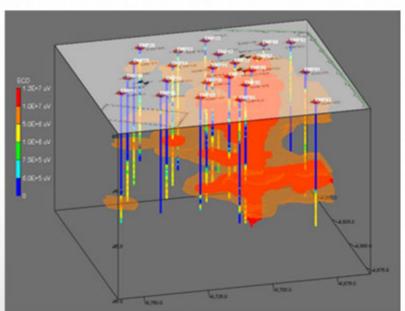




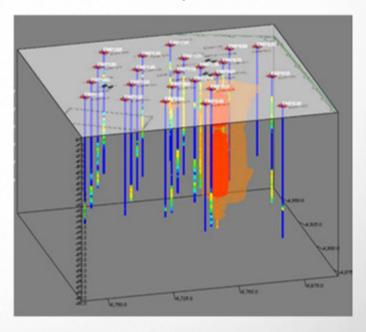
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Pre-injection



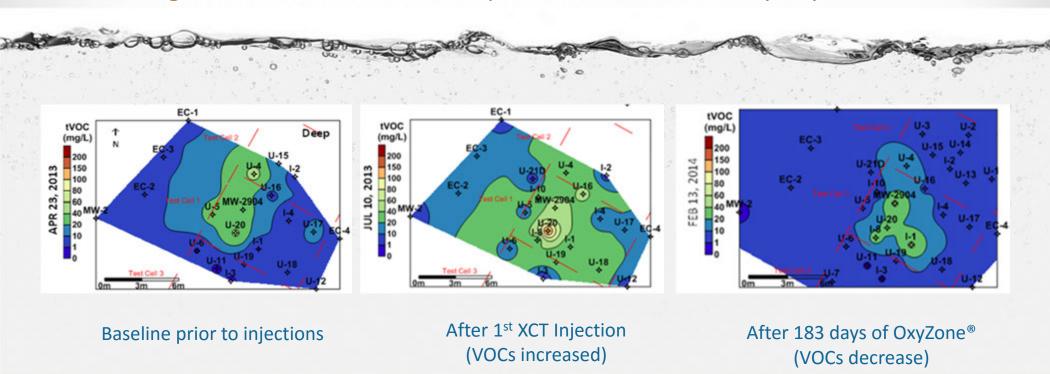
Post-injection





Impact of XCTTM on Total VOC Concentration in Groundwater

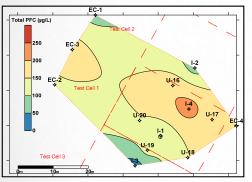
XCT[™] is a patented biodegradable carbohydrate mixture to enhance the solubility of organic contaminants for subsequent efficient oxidation by OxyZone[®]





Field Demonstration Groundwater Results for PFAS

April 2013



PFOS (µg/L)

Test Cell 2

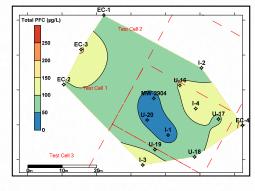
Test Cell 1

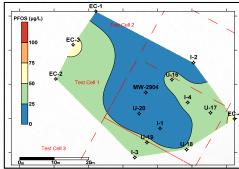
Test Cell 3

Test Cell 3

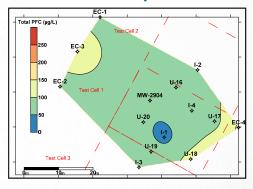
OxyZone®
Injections:
May &
JulyAugust
2013

October 2013

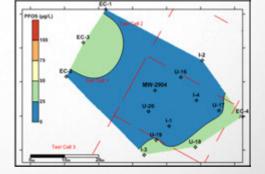




February 2014



Total PFAS



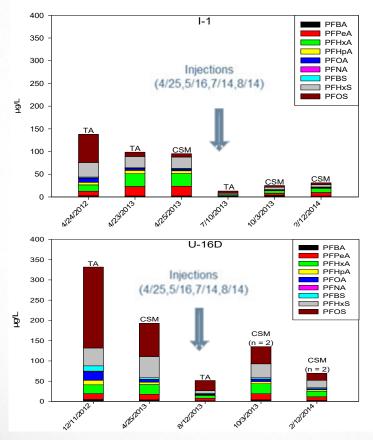
PFOS only

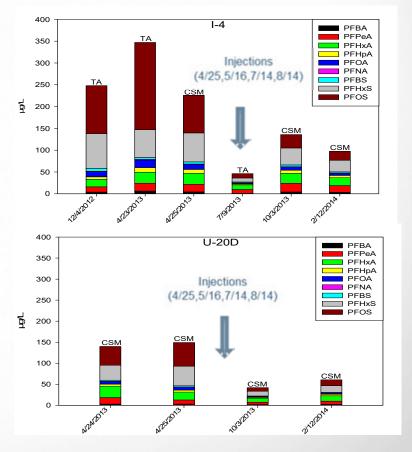


Field Demonstration Results for PFAS

Deep wells within injection test cell

Statistically significant (p=0.005) decrease in PFAS concentrations after injections





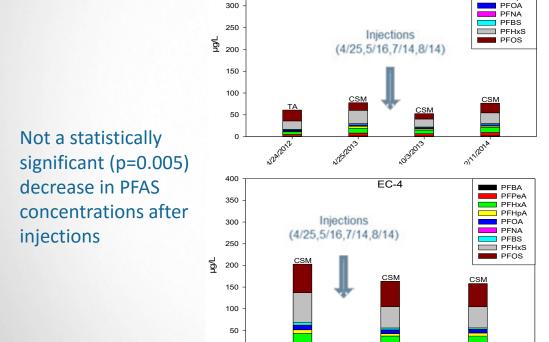


Field Demonstration Results for PFAS

Deep wells **outside** injection test cell

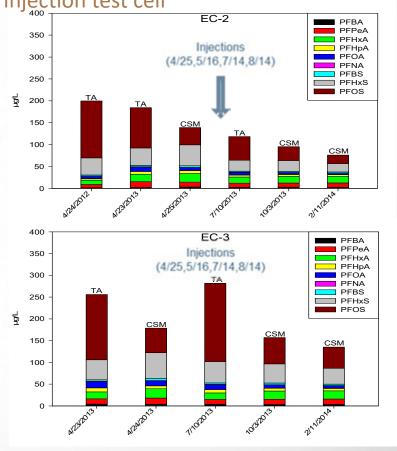
PFBA
PFPeA
PFHxA

☐ PFHpA



400

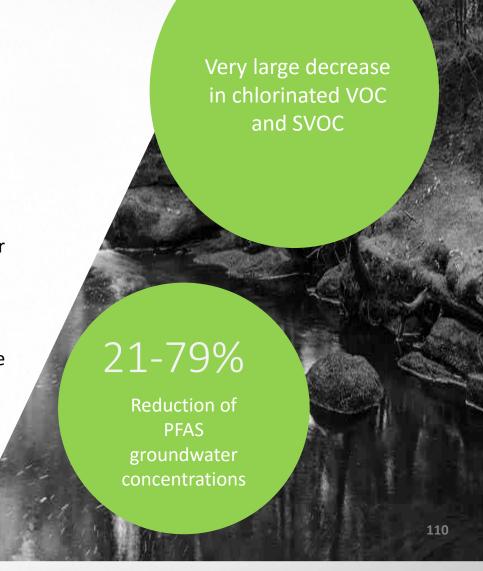
350





Field Demonstration Results

- Based on MIPs data, overall VOC and SVOC contaminant mass significantly reduced in and around Test Cell where OxyZone[®] was injected
- 9 different PFAS were discovered during baseline testing and monitoring
- Groundwater data analysis supported a statistically significant reduction in PFAS concentrations (21% to 79%) in groundwater
- Indicative that OxyZone® processes successfully degraded PFAS in-situ in the presence of high concentrations of other organics
- Statistical comparison of wells within Test Cell to those outside Test Cell showed PFAS concentrations decreased within Test Cell, not outside
- Groundwater concentrations of conservative tracer chloride showed no (dilution) impact from injections





Confirmatory Bench Scale Treatability Testing of PFAS

EnChem Engineering

OxyZone® process performed on:

- contaminated groundwater from the Fire Training Area
- distilled –deionized water
- Tested both unspiked & spiked PFOA & PFOS



Bench Scale Treatability Testing on Spiked DI and

Groundwater (JBLE)

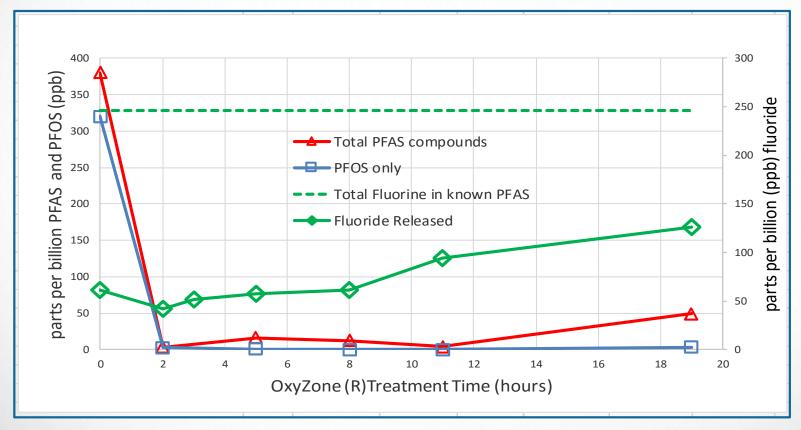
Spiked Deionized Water (after 2 hours OxyZone® treatment)					
Specific PFAS	Initial concentration	Final concentration	Net Change		
PFOS: (8 carbon sulfonate)	93 ppb	< 1 ppb	99% decrease		
PFOA: (8 carbon acid)	83 ppb	< 1 ppb	99% decrease		
PFHpS (7 carbon sulfonate)	4 ppb	< 0.4 ppb	99% decrease		
PFHxA (6 carbon acid)	6 ppb	6 ppb	no change		

Specific PFAS	Initial concentration	Intermediate (3 hrs.) concentration	Final (6 hrs.) Concentration	Net Change
PFOS: (8 carbon sulfonate)	138 ppb	25 ppb	3 ppb	95% decrease
PFOA: (8 carbon acid)	33 ppb	22 ppb	6 ppb	97% decrease
PFHpS: (7 carbon sulfonate)	7 ppb	4 ppb	0.4 ppb	97% decrease
PFHpA: (7 carbon acid)	6 ppb	< 0.4 ppb	< 0.4 ppb	67% decrease
PFHxA: (6 carbon acid)	15 ppb	43 ppb	30 ppb	net increase
PFHxS: (6 carbon sulfonate)	68 ppb	99 ppb	14 ppb	79% decrease
PFPeA: (5 carbon acid)	11 ppb	< 2 ppb	< 2 ppb	91% decrease
PFBS: (4 carbon sulfonate)	9 ppb	14 ppb	10 ppb	no change
PFBA: (4 carbon acid)	3 ppb	6 ppb	5 ppb	small increase



Bench Scale Lab Results #1:

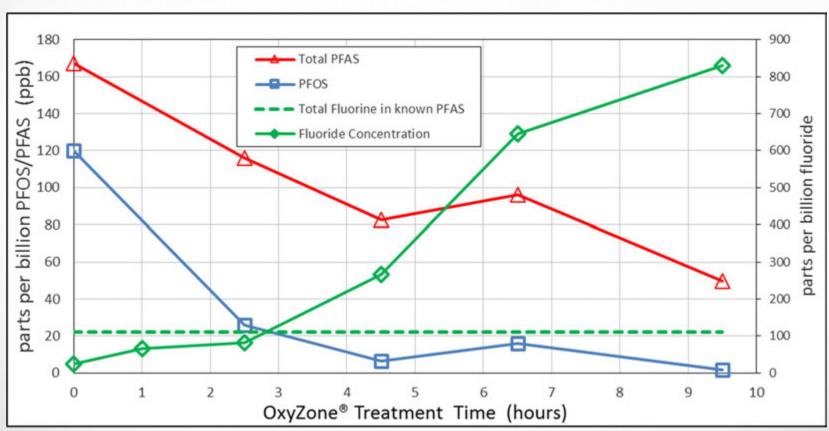
Actual AFFF Site Contaminated Groundwater – 39% Fluoride released





Bench Scale Lab Results: #2

Actual AFFF Site Contaminated Groundwater – High Undetected PFAS – 750% Fluoride Recovery



EnChem Engineering, Inc.

Case Study Results

Bench Scale Testing

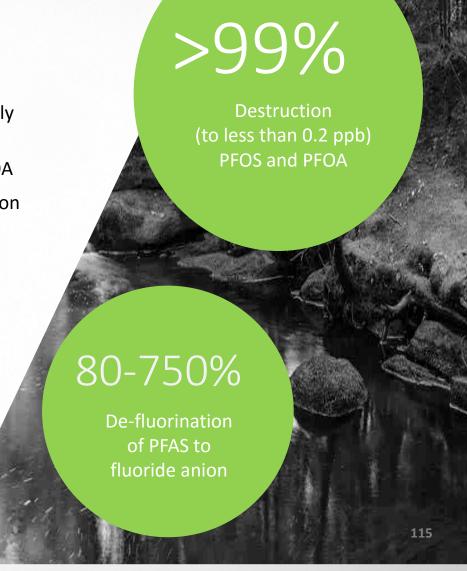
 Subsequent evaluation of OxyZone® in the laboratory repeatedly confirmed PFAS destruction and de-fluorination

Up to 99.9% destruction (to less than 0.2 ppb) of PFOS and PFOA

80 - 750% defluorination of PFAS organofluorine to fluoride anion

Conclusion

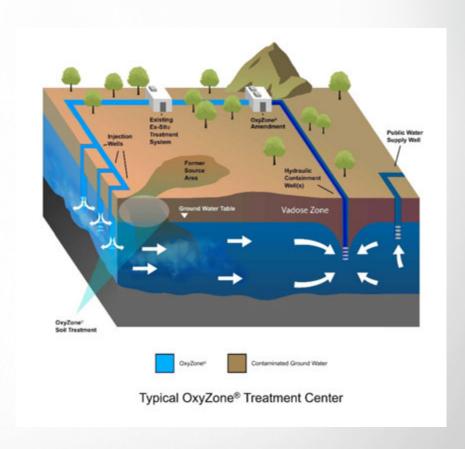
Results indicate that OxyZone® has the capability to decrease PFAS to very low concentrations, either in-situ or ex-situ.





OxyZone® PFAS Remediation Options

- ➤ In-Situ Recirculation Option (depicted on right):
- ➤ Above-ground Treatment Reactor
- Enclosed Soil Reactor for Vadose Zone Soils
- ➤ Horizontal Injection Wells on Plume Transec
- ➤ Vertical Injection Wells on Plume Transect





OxyZone® Field Demonstration

Acknowledgements

• Tom Boving, Ph.D., Co-Principal Investigator, and Dylan Eberle, Ph.D., University of Rhode Island (for Field Demonstration effort)



 AFCEC, for funding the Field Demonstration Project, FA8903-11-C-8804: Chemical Oxidation and Inclusion Technology for Expedited Soil and Groundwater Remediation



Last Thoughts

- ☐ PFAS on most people's radar screen for just a few years
- ☐ PFAS remediation very challenging:
 - ➤ Moving targets which PFAS need to be remediated and to what concentrations?
 - ➤ Large number of chemicals
 - > Low concentrations of concern
 - ➤ Many data gaps and analytical difficulties
 - ➤ Complexity due to chemical transformations
 - > Thin track record of many remediation technologies



Last Thoughts

- ☐ Technologies that are currently most promising for PFAS
 - > Filtration (Nano-filtration, reverse osmosis)
 - > Adsorbents
 - ➤ Ion exchange / adsorption resins
 - Chemical oxidation / reduction
- ☐ Treatability studies should be considered:
 - > Select the best technology(s)
 - Function of PFAS concentrations
 - ➤ Optimize remediation design
 - ➤ Minimize the risk of unintended consequences



Question and Answers

For any questions that we cannot get to during the Q/A period, please feel free to contact the presenters:

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